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**14. ABSTRACT**

A new class of perfluorocyclobutyl (PFCB) polymers covalently functionalized with polyhedral oligomeric silsesquioxnes (POSS) is presented. Three discreetly functionalized POSS monomers possessing thermally reactive trifluorovinyl aryl ethers (TFVE) were prepared in good yields. The POSS TFVE monomers were prepared by initial corner capping of cyclopentyl (-C5H9), iso-butyl (-CH2CH(CH3)2), or trifluoropropyl (-CH2CH2CF3) functionalized POSS trisilanols with acetoxyethyltrichlorsilane followed by sequential acid-catalyzed deprotection and coupling with 4-(trifluorovinyloxy)benzoic acid. TFVE functionalized POSS monomers were thermally polymerized with 4,4'-bis(4-trifluorovinyloxy)biphenyl or 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane monomers via a condensate-free, [2+2] step-growth polymerization. The polymerization afforded solution processable PFCB polymers with POSS macromers installed on the polymer chain ends. POSS monomers and their corresponding copolymers were characterized by 1H, 13C, 19F, and 29Si NMR, GPC, ATR-FTIR, and elemental combustion analysis. GPC trace analysis showed agreeable number-average molecular weight for various weight percent of iso-butyl and trifluoropropyl chain terminated POSS PFCB copolymers. DSC analysis showed the introduction of increasing POSS weight percent in the endcapped PFCB copolymers lowers glass transition temperatures as high as 31 °C. On the other hand, the trifluoropropyl POSS endcapped PFCB polymer glass transition temperature was unaffected when copolymerized with the more fluorinated 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane monomer. TGA analysis of POSS PFCB copolymers showed step-wise decomposition of copolymers resulting from the initial degradation of the POSS cages at 297−355 °C in nitrogen and air which was confirmed by pyrolysis coupled with GC−MS. This initial weight loss was proportional to the weight percent POSS incorporated into the polymer. The balance of decomposition was observed at 450−563 °C in nitrogen and air which is higher than the PFCB homopolymers in most cases. Polymer surface characterization was performed on spin cast transparent, flexible films. These composite films exhibited good POSS dispersion within the matrix PFCB polymer as was shown by TEM analysis.

**15. SUBJECT TERMS**

perfluorocyclobutyl (PFCB) polymer; polyhedral oligomeric silsesquioxanes; POSS

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# Synthesis, characterization, and properties of chain terminated polyhedral oligomeric silsesquioxane-functionalized perfluorocyclobutyl aryl ether copolymers

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**Abstract**

A new class of perfluorocyclobutyl (PFCB) polymers covalently functionalized with polyhedral oligomeric silsesquioxane (POSS) is presented. Three discreetly functionalized POSS monomers possessing thermally reactive trifluorovinyl aryl ether (TFVE) were prepared in good yields. The POSS TFVE monomers were prepared by initial corner-capping of cyclopentyl ($-C_5H_9$), *iso*-butyl ($-CH_2CH(CH_3)_2$), or trifluoropropyl ($-CH_2CH_2CF_3$) functionalized POSS trisilanols with acetoxyethyltrichlorosilane followed by sequential acid-catalyzed deprotection and coupling with 4-(trifluorovinyloxy)benzoic acid. TFVE-functionalized POSS monomers were thermally polymerized with 4,4′-bis(4-trifluorovinyloxy)biphenyl or 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane monomers *via* a condensate-free, [2 + 2] step-growth polymerization. The polymerization afforded solution processable PFCB polymers with POSS macromer installed on the polymer chain ends. POSS monomers and their corresponding copolymers were characterized by $^{1}H$, $^{13}C$, $^{19}F$, and $^{29}Si$ NMR, GPC, ATR-FTIR, and elemental combustion analysis. GPC trace analysis showed agreeable number-average molecular weight for various weight percent of cyclopentyl or *iso*-butyl and trifluoropropyl chain terminated POSS PFCB copolymers. DSC analysis showed the introduction of increasing POSS weight percent in the endcapped PFCB copolymers lowers the glass transition temperatures as high as 31 °C. On the other hand, the trifluoropropyl POSS endcapped PFCB polymer glass transition temperature was unaffected when copolymerized with the more fluorinated 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane monomer. TGA analysis of POSS PFCB copolymers showed step-wise decomposition of copolymers resulting from the initial degradation of the POSS cages at 297–355 °C in nitrogen and air which was confirmed by pyrolysis coupled with GC–MS. This initial weight loss was proportional to the weight percent of POSS incorporated into the polymer. The balance of decomposition was observed at 450–563 °C in nitrogen and air which is higher than the PFCB homopolymers in most cases. Polymer surface characterization was performed on spin cast transparent, flexible films. These composite films exhibited good POSS dispersion within the matrix PFCB polymer as was shown by TEM analysis.


*Keywords:* Perfluorocyclobutyl (PFCB) polymer; Polyhedral oligomeric silsesquioxanes; POSS

## 1. Introduction

Fluoropolymers are important for a broad range of advanced material applications [1]. Introducing fluorine into a polymer backbone creates an interesting paradox in terms of desired properties. In one sense, highly fluorinated polymers are desired due to their inherent high degree of chemical resistance, superior thermal stability, excellent insulating ability, and low surface energy. However, perfluorinated polymers, like poly(tetrafluoroethylene) (PTFE), are intrinsically highly crystalline and thus present challenges in terms of high processing cost. Therefore, interest continues to develop next generation fluoropolymers motivated by the need to overcome processing limitations while maintaining performance-enhancing properties.

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Perfluorocyclobutyl (PFCB) polymers [2] have gained much interest as processable, semi-fluorinated polymers advancing a multitude of technology corridors such as high performance optics [3], polymer light-emitting diodes (PLEDs) [4], atomic oxygen (AO) resistant coatings [5], polymeric proton exchange membranes (PEMs) for fuel cells [6], high temperature fluorosilicones [7], and liquid-crystalline polymers [8]. PFCB polymers are prepared by condensate-free, step-growth thermal [2 + 2] dimerization of trifluorovinyl aryl ether (TFVE) monomers (Scheme 1) [9]. The cycloaddition event has been studied by Raman spectroscopy and was shown to proceed *via* a biradical intermediate producing nearly exclusive formation of 1,4-perfluorocyclobutyl aryl ether rings in the chain extended polymer system [10]. The stereo-random nature of the PFCB aryl ether linkage typically affords an amorphous thermoplastic attractive for solution processing. As a consequence of the aromatic ether structure, PFCB polymers have an intrinsically high glass transition temperature and possess a high degree of thermal stability in air. TFVE monomers are easily functionalized from versatile organometallic reagents derived from 4-bromo(trifluorovinyloxy)benzene as a commercial starting material [11].

Since their seminal inception by Vogt and Scott [12], polyhedral oligomeric silsesquioxane (POSS) compounds comprised of a functionalized silicon–oxygen core framework have received much interest as robust nanometer-sized building blocks for the development of high performance materials [13]. POSS incorporation, either in polymer blends or covalently bound as copolymers, produces hybrid organic–inorganic composites improving the properties of the virgin polymer such as glass transition temperature, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen resistance.

Octa(aminophenyl)silsesquioxane (OAPS) with TFVE moieties installed on each apex silicon of the POSS $T_8$ cage has been reported [14]. Thermal polymerization of the TFVE-functionalized OAPS with PFCB oligomers produced crosslinked materials possessing excellent thermal stability while retaining the optical integrity of the matrix polymer. Similarly, PFCB thermoplastics as well as thermosets possessing siloxane linkages have also been prepared [7] contributing to the established class of fluorosilicones as lubricants and adhesives [15].

In this report, our aim is to expand the utility of PFCB polymers by introducing covalently bound ceramic-like POSS cages while maintaining the processability of the semi-fluorinated matrix. We anticipate the introduction of POSS cages attached on the polymer chain ends would produce hybrid polymers with controlled molecular weight that could enhance bulk properties such as hydro- and oleophobicity, thermal stability, mechanical integrity, tunable refractive index, low dielectric values, and improved gas permeability.

## 2. Experimental section

### 2.1. General information and materials

Chemicals and solvents were purchased from Sigma–Aldrich and purified according to reported procedures unless otherwise stated [16]. POSS triols **1** and **2** were donated by the Air Force Research Laboratory, Edwards Air Force Base and are commercially available through Hybrid Plastics. 4,4′-Bis(4-trifluorovinyloxy)biphenyl (**4**) and 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane (**5**) were donated by Tetramer Technologies, L.L.C. and are commercially distributed through Oakwood Chemicals, Inc. All reactions were carried out under ultra-high purity nitrogen. Flasks and syringes were flamed-dried under vacuum and allowed to cool in a desiccator filled with Drierite prior to use.

### 2.2. Instrumentation

#### 2.2.1. NMR spectrometry

$^{1}H$, $^{13}C$ (proton decoupled), $^{19}F$, and $^{29}Si$ NMR data were obtained on a JEOL Eclipse$^{+}$ 300 and chemical shifts were reported in part per million ($\delta$ ppm). $^{1}H$ NMR data were internally referenced to tetramethylsilane ($\delta$ 0.0), $^{13}C$ NMR chemical shifts were reported relative to the center peak of the multiplet for $CDCl_3$ ($\delta$ 77.0 (t)), and $^{19}F$ NMR was referenced to $CFCl_3$. $^{29}Si$ NMR data were referenced to tetramethylsilane ($\delta$ 0.0) and were recorded with inverse-gated proton decoupling with a six second pulse delay.

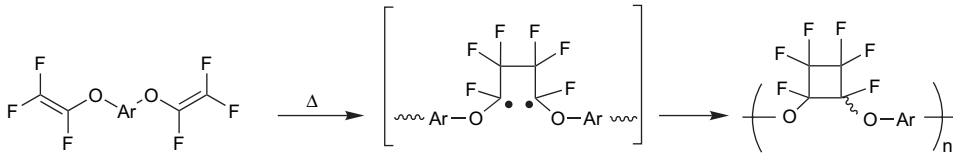
#### 2.2.2. IR spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis of neat samples was performed on a ThermoNicolet Magna IR 550 FTIR spectrophotometer.

#### 2.2.3. Chromatography

Gel permeation chromatography (GPC) data were collected in $CHCl_3$ using polystyrene as a standard (Polymer Labs Easical PS-2) using a Waters 2690 Alliance System with UV–vis detection. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. See Table 1 for polymer molecular weights.

Gas chromatography (GC) coupled with mass spectrometry (MS) was performed on a Shimadzu GC-17A gas chromatograph coupled with a Shimadzu QP5000 mass spectrometer




Scheme 1. Thermal [2 + 2] cyclopolymerization of trifluorovinyl aryl ethers.

Table 1
Selected properties of polymers

| Polymer | wt% POSS | mol% POSS | | $M_n \times 10^{-3}$ [b] | $M_w/M_n$ | $T_g$ [c] (°C) |
|---|---|---|---|---|---|---|
| | | Calculated | Found[a] | GPC | | |
| **poly4** | 0 | 0.0 | – | 25.0 | 2.1 | 140 |
| **1c-*co*-4** | 10 | 3.7 | 2.0 | 5.7[d] | 2.0 | 122 |
| **1c-*co*-4** | 20 | 7.9 | 6.5 | 6.4[d] | 2.2 | 119 |
| **2c-*co*-4** | 10 | 4.0 | 2.3 | 10.3 | 1.8 | 124 |
| **2c-*co*-4** | 20 | 8.5 | 8.0 | 12.6 | 2.3 | 109 |
| **3c-*co*-4** | 10 | 3.2 | 1.7 | 22.2 | 3.0 | 138 |
| **3c-*co*-4** | 20 | 6.9 | 3.6 | 28.8 | 4.3 | 131 |
| **poly5** | 0 | 0.0 | – | 11.2 | 2.1 | 97 |
| **3c-*co*-5** | 20 | 8.5 | 4.4 | 8.8 | 1.6 | 100 |

[a] Measured by $^1$H NMR using integration ratio of aryl to POSS alkyl peaks.
[b] GPC in $CHCl_3$ using polystyrene as standard.
[c] DSC (10 °C/min) in nitrogen determined from third re-heating cycle.
[d] Average of two polymerizations.

(EI at 70 eV) with an initial temperature of 60 °C at a ramp of 10 °C/min.

### 2.2.4. Thermal analysis

Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and Mettler–Toledo 851 instrument, respectively. Glass transitions temperatures ($T_g$) of polymers were obtained from the third heating cycle using DSC analysis at a temperature ramp of 10 °C/min. See Table 1 for glass transition temperature ($T_g$) and Table 2 for thermal decomposition temperature ($T_d$) in nitrogen and air of polymers. Melting points were measured using either DSC or a Mel-Temp melting point apparatus. Combustion analysis was obtained from Atlantic Microlab, Inc. High resolution mass spectra of **3c** was obtained at the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois-Urbana Champaign using a high resolution Micromass FAB 70-SE-4F. Pyrolysis analysis was carried out on Frontier Lab single-shot at 500 °C interfaced with the GC–MS.

### 2.2.5. Microscopy

Transmission electron microscopy (TEM) micrographs were obtained from a Hitachi H9500 with an accelerating voltage of 300 kV at the Clemson University Electron Microscope Facility. Samples were prepared by casting polymer solutions from THF onto copper TEM grids and allowed to dry in a desiccator for 24 h prior to use.

Table 2
Summary of thermal decomposition of copolymers

| Polymer | wt% POSS | In $N_2$ | | | In air | |
|---|---|---|---|---|---|---|
| | | $T_d$[a] (°C) | Initial weight loss (%) | Char (%) | $T_d$[a] (°C) | Initial weight loss (%) |
| **poly4** | 0 | 450 | – | 45 | 446 | – |
| **1c-*co*-4** | 10 | 322, 464 | 6.3 | 41 | 330, 489 | 3.0 |
| **1c-*co*-4** | 20 | 316, 518 | 14.6 | 37 | 355, 479 | 7.0 |
| **2c-*co*-4** | 10 | 304, 461 | 6.8 | 40 | 306, 563 | 5.9 |
| **2c-*co*-4** | 20 | 307, 521 | 14.2 | 54 | 297, 558 | 12.1 |
| **3c-*co*-4** | 10 | 325, 450 | 10.0 | 30 | 300, 450 | 10.0 |
| **3c-*co*-4** | 20 | 319, 467 | 15.0 | 32 | 310, 460 | 12.6 |
| **poly5** | 0 | 466 | – | 25 | 457 | – |
| **3c-*co*-5** | 20 | 318, 474 | 12.2 | 20 | 310, 460 | 12 |

[a] TGA onset at 10 °C/min of chain extended polymers.

### 2.3. Synthesis of *1a*

Acetoxyethyltrichlorosilane (2.1 mL, 12.0 mmol) was added drop wise to a stirred solution of trisilanolcyclopentyl-POSS **1** (10 g, 11.4 mmol) and triethylamine (5.8 mL, 42.0 mmol) in THF (120 mL). After 5 h, the solution was filtered and concentrated under vacuum. The solid was then dispersed in methanol (200 mL), filtered, washed repeatedly with methanol (2 × 100 mL), and dried under vacuum to afford **1a** as a white, free-flowing powder (10.6 g, 94%). ATR-FTIR (neat): $\nu$ 2953 (w), 1464 (w), 1229 (w), 1087 (vs), 1035 (m), 838 (w), 744 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 4.17 (t, $J = 6.0$ Hz, 2H), 2.02 (s, 3H), 1.86–1.38 (m, 56H), 1.07 (t, $J = 6.0$ Hz, 2H), 1.04–0.92 (m, 7H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 171.2, 61.3, 27.4, 27.1, 22.3, 21.2, 13.5; $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −65.9, −66.0, −69.2 (3:4:1). Anal. Calcd for $C_{39}H_{70}O_{14}Si_8$: C, 47.43; H, 7.14. Found: C, 47.23; H, 7.31.

### 2.4. Synthesis of *1b*

Concentrated $H_2SO_4$ (0.8 mL) was added to **1a** (4 g, 4.05 mmol) dissolved in methanol (200 mL) and chloroform (200 mL). After 48 h, the solution was concentrated under vacuum. The crude concentrate was redissolved in ethyl acetate (200 mL), washed repeatedly with water (2 × 100 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum to afford **1b** as a white crystalline powder (3.7 g, 97%). ATR-FTIR (neat): $\nu$ 2948 (m), 2864 (m), 1086 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 4.17 (t, $J = 15.5$ Hz, 2H), 1.95–1.41 (m, 56H), 1.08–0.92 (m, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 58.9, 27.4, 27.1, 22.3, 17.7; $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −65.9, −68.1 (7:1). Anal. Calcd for $C_{37}H_{68}O_{13}Si_8$: C, 47.00; H, 7.25. Found: C, 46.75; H, 7.28.

### 2.5. Synthesis of *1c*

4-(Trifluorovinyloxy)benzoic acid (254 mg, 1.16 mmol) was added to a solution of dicyclohexylcarbodiimide (DCC) (254 mg, 1.27 mmol), 4-(dimethyl-amino)pyridinium 4-toluenesulfonate (DPTS) (107 mg, 0.35 mmol), and **1b** (1 g, 1.06 mmol) in dichloromethane (20 mL). After 24 h, the solution was filtered and concentrated under vacuum. Purification of the residue by flash chromatography on silica gel using 5% ethyl acetate–95% hexanes (v/v) for elution afforded **1c** as a white solid (1 g, 83%). $R_f$ 0.50 (5% ethyl acetate–95% hexanes (v/v)); mp >260 °C; ATR-FTIR (neat): $\nu$ 2949 (m), 1723 (w), 1271 (w), 1084 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 8.09 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.6$ Hz, 2H), 4.45 (t, $J = 7.9$ Hz, 2H), 1.78–0.84 (m, 65H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6, 158.2, 132.0, 127.5, 115.4, 62.1, 29.8, 27.4, 27.0, 22.3, 13.5; $^{19}$F NMR ($CDCl_3$, 283 MHz):

$\delta$ −118.7 (dd, $J = 95.5$, 55.4 Hz, *cis*-CF=C$F_2$, 1F), −125.5 (dd, $J = 111.9$, 95.5 Hz, *trans*-CF=C$F_2$, 1F), −134.2 (dd, $J = 111.9$, 52.4 Hz, C$F$=C$F_2$, 1F); $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −65.9, −68.0, −69.1 (4:3:1). Anal. Calcd for $C_{46}H_{71}F_3O_{15}Si_8$: C, 48.22; H, 6.25; F, 4.97. Found: C, 48.22; H, 6.25; F, 4.97. GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution with $M_n = 842$ ($M_w/M_n = 1.0$).

### 2.6. Synthesis of **2a**

Trisilanolisobutyl-POSS **2** (9 g, 11.4 mmol) was used following the procedure outlined for the preparation of **1a** to obtain **2a** as a white solid (9.1 mg, 88%). ATR-FTIR (neat): $\nu$ 2953 (w), 1745 (w), 1229 (w), 1085 (vs), 1037 (m), 838 (w), 739 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 4.17 (t, $J = 8.6$ Hz, 2H), 2.01 (s, 3H), 1.91−1.78 (m, 7H), 1.08 (t, $J = 8.6$ Hz, 2H), 1.01−0.93 (m, 42H), 0.60−0.58 (m, 14H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 171.0, 61.1, 25.8, 23.9, 22.5, 21.1, 13.5; $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −67.0, −67.4, −70.0 (3:4:1). Anal. Calcd for $C_{32}H_{70}O_{14}Si_8$: C, 42.54; H, 7.81. Found: C, 42.50; H, 7.96.

### 2.7. Synthesis of **2b**

Compound **2a** (5.5 g, 6.09 mmol) was used following the procedure outlined for the preparation of **1b** to obtain **2b** as a white solid (4.1 mg, 80%). ATR-FTIR (neat): $\nu$ 2948 (m), 2864 (m), 1086 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 4.17 (t, $J = 7.9$ Hz, 2H), 1.92−1.78 (m, 7H), 1.63 (s, OH), 1.06 (t, $J = 7.8$ Hz, 2H), 0.96−0.94 (m, 42H), 0.61−0.59 (m, 14H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 58.8, 25.7, 23.9, 22.5, 17.8; $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −67.1, −67.3, −69.1 (3:4:1). Anal. Calcd for $C_{30}H_{68}O_{13}Si_8$: C, 41.82; H, 7.96. Found: C, 41.20; H, 8.11.

### 2.8. Synthesis of **2c**

Compound **2b** (5.5 g, 6.09 mmol) was used following the procedure outlined for the preparation of **1c** to obtain **2c** as a white solid (1.8 mg, 73%). Mp 75−77 °C; ATR-FTIR (neat): $\nu$ 2953 (m), 1725 (w), 1273 (w), 1086 (vs) 740 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 8.09 (d, $J = 8.9$ Hz, 2H), 7.12 (d, $J = 8.9$ Hz, 2H), 4.45 (t, $J = 7.9$ Hz, 2H), 1.85−1.82 (m, 7H), 1.24 (t, $J = 7.9$ Hz, 2H), 0.97−0.93 (m, 42H), 0.59 (t, $J = 7.5$ Hz, 14H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 165.5, 158.2, 132.0, 127.5, 115.5, 61.9, 25.8, 23.9, 22.6, 13.5; $^{19}$F NMR ($CDCl_3$, 283 MHz): $\delta$ −118.7 (dd, $J = 95.5$, 55.4 Hz, *cis*-CF=C$F_2$, 1F), −125.4 (dd, $J = 111.9$, 95.5 Hz, *trans*-CF=C$F_2$, 1F), −134.4 (dd, $J = 111.9$, 52.4 Hz, C$F$=C$F_2$, 1F); $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −67.0, −67.3, −69.9 (3:4:1). Anal. Calcd for $C_{39}H_{71}F_3O_{15}Si_8$: C, 44.12; H, 6.74; F, 5.37. Found: C, 43.98; H, 6.99; F, 5.09. GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution with $M_n = 1052$ ($M_w/M_n = 1.0$).

### 2.9. Synthesis of **3c**

Hepta(3,3,3-trifluoropropyl)-tricycloheptasiloxane trisodium silanolate **3** (3.0 g, 3.42 mmol) was used for the preparation of **3a** and **3b** previously reported by Fukada et al. [18]. Compound **3b** was used following the procedure outlined for the preparation of **1c** to obtain **3c** as a white solid (1.85 mg, 40%). Mp 75−76 °C; ATR-FTIR (neat): $\nu$ 2954 (m), 1723 (m), 1216 (vs), 1112 (vs), 903 (w), 837 (w) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 8.09 (d, $J = 8.9$ Hz, 2H), 7.13 (d, $J = 8.9$ Hz, 2H), 4.45 (t, $J = 7.9$ Hz, 2H), 2.20−2.05 (m, 14H), 1.33 (t, $J = 7.9$ Hz, 2H), 0.96−0.86 (m, 14H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 165.3, 131.9, 128.9, 126.9, 125.3, 115.6, 60.7, 28.3, 27.9, 27.5, 27.0, 4.01; $^{19}$F NMR ($CDCl_3$, 283 MHz): $\delta$ −68.6 (s, $CH_2CH_2CF_3$, 21F), −118.5 (dd, $J = 95.5$, 55.4 Hz, *cis*-CF=C$F_2$, 1F), −125.4 (dd, $J = 111.9$, 95.5 Hz, *trans*-CF=C$F_2$, 1F), −134.5 (dd, $J = 111.9$, 52.4 Hz, C$F$=C$F_2$, 1F); $^{29}$Si NMR ($CDCl_3$, 59 MHz): $\delta$ −67.5, −67.6, −68.6 (4:3:1). Anal. Calcd for $C_{32}H_{36}F_{24}O_{15}Si_8$: C, 28.66; H, 2.71; F, 33.99. Found: C, 29.86; H, 2.86; F, 33.01. HRMS-FAB (*m/z*) $[M + H]^+$ Calcd for $C_{32}H_{36}F_{24}O_{15}Si_8$: 1340.9900; found: 1340.9907. GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution with $M_n = 1060$ ($M_w/M_n = 1.0$).

### 2.10. Preparation of copolymer ***1c-co-4***

In a flame-dried vacuum-sealed glass ampoule, a specified amount of **1c** and **4** were heated to 180 °C for 48 h. After cooling and opening the ampoule, the polymer was dissolved in a minimal amount of THF and precipitated in methanol, filtered, washed repeatedly with methanol, and dried under vacuum to afford a pale yellow-white fibrous solid in nearly quantitative yield. ATR-FTIR (neat): $\nu$ 2950 (w), 1606 (w), 1496 (vs), 1196 (vs), 1109 (vs), 957 (vs), 823 (m) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.48−7.46 (m, 6H), 7.24−7.16 (m, 6H), 4.10 (t, $J = 7.8$ Hz, 2H), 1.80−0.85 (m, 65H); $^{19}$F NMR ($CDCl_3$, 283 MHz): $\delta$ −128.0 to −131.4 (m, cyclobutyl-$F_6$).

### 2.11. Preparation of copolymer ***2c-co-4***

Compounds **2c** and **4** were used following the procedure outlined for the preparation of **1c-*co*-4** to obtain **2c-*co*-4** as a pale yellow-white fibrous solid in nearly quantitative yield. ATR-FTIR (neat): $\nu$ 29570 (w), 1606 (w), 1495 (vs), 1301 (s), 1193 (vs), 1107 (s), 953 (vs), 821 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.60−7.45 (m, 6H), 7.26−7.18 (m, 6H), 3.76−3.72 (m, 2H), 1.87−1.83 (m, 2H), 1.60−1.54 (m, 7H), 0.96−0.92 (42H), 0.61−0.57 (m, 14H); $^{19}$F NMR ($CDCl_3$, 283 MHz): $\delta$ −126.5 to −131.2 (m, cyclobutyl-$F_6$).

### 2.12. Preparation of copolymer ***3c-co-4***

Compounds **3c** and **4** were used following the procedure outlined for the preparation of **1c-*co*-4** to obtain **3c-*co*-4** as a pale yellow-white, fibrous solid in nearly quantitative yield.

ATR-FTIR (neat): $\nu$ 2926 (w), 1606 (m), 1496 (vs), 1305 (vs), 1199 (vs), 962 (vs), 851 (s), 600 (m) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 7.60–7.45 (6H), 7.23–7.03 (6H), 4.42 (t, $J = 7.9$ Hz, 2H), 2.17–2.08 (m, 14H), 1.26 (t, $J = 7.9$ Hz, 2H), 0.96–0.86 (m, 14H); $^{19}F$ NMR ($CDCl_3$, 283 MHz): $\delta$ −68.5 (21F), −126.4 to −131.2 (m, cyclobutyl-$F_6$).

### 2.13. Preparation of copolymer *3c-co-5*

Compounds **3c** and **5** were used following the procedure outlined for the preparation of **1c-*co*-4** except heating was prolonged for 96 h to obtain **3c-*co*-5** as a pale yellow-white, fibrous solid in nearly quantitative yield. ATR-FTIR (neat): $\nu$ 2950 (w), 1512 (m), 1174 (vs), 1117 (s), 1305 (vs), 962 (s), 831 (s) $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 7.40–7.06 (m, 12H), 4.44 (t, $J = 7.9$ Hz, 2H), 2.18–2.11 (m, 14H), 1.29 (t, $J = 7.9$ Hz, 2H), 0.96–0.86 (m, 14H); $^{19}F$ NMR ($CDCl_3$, 283 MHz): $\delta$ −63.9 (6F), −68.6 (21F), −127.2 to −132.8 (m, cyclobutyl-$F_6$).

### 2.14. Preparation of homopolymers *poly4* and *poly5*

In a flame-dried vacuum-sealed glass ampoule, a specified amount of **4** or **5** was heated to 180 °C for 48 h. After cooling and opening the ampoule, the polymer was dissolved in a minimal amount of THF and precipitated in methanol, filtered, washed repeatedly with methanol, and dried under vacuum to afford a white fibrous solid in nearly quantitative yield. Their characterization has been previously reported [9a,17].

## 3. Results and discussion

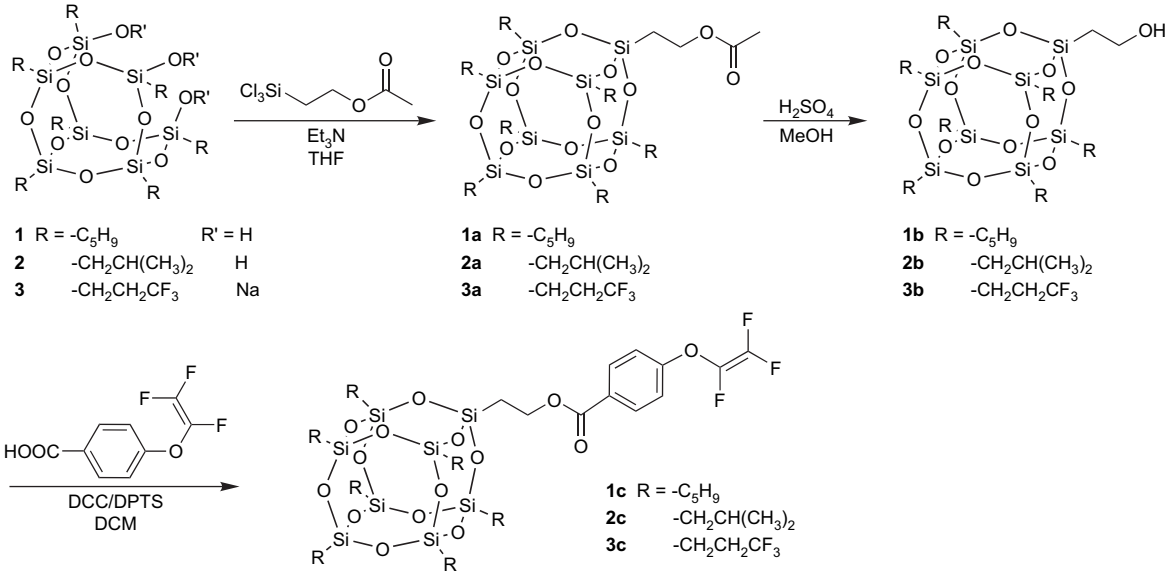
### 3.1. Monomer synthesis

POSS-functionalized TFVE monomers **1c** and **2c** were prepared from commercially available functionalized POSS triols **1** and **2** (Scheme 2). POSS trisodium silanolate **3** was synthesized *via* the hydrolytic condensation of trifluoropropyltrimethoxysilane under basic conditions in the presence of potassium hydroxide [18]. Initial corner-capping *via* the condensation of POSS triols **1**–**3** with acetoxyethyltrichlorosilane afforded the POSS $T_8$ cages **1a**–**3a**. POSS alcohols **1b**–**3b** were produced in nearly quantitative yield by deprotection of the POSS esters **1a**–**3a** under mild acidic conditions. Dicyclohexylcarbodiimide (DCC) coupling with 4-(trifluorovinyloxy)benzoic acid produced the desired POSS-functionalized TFVE monomers **1c**–**3c**.

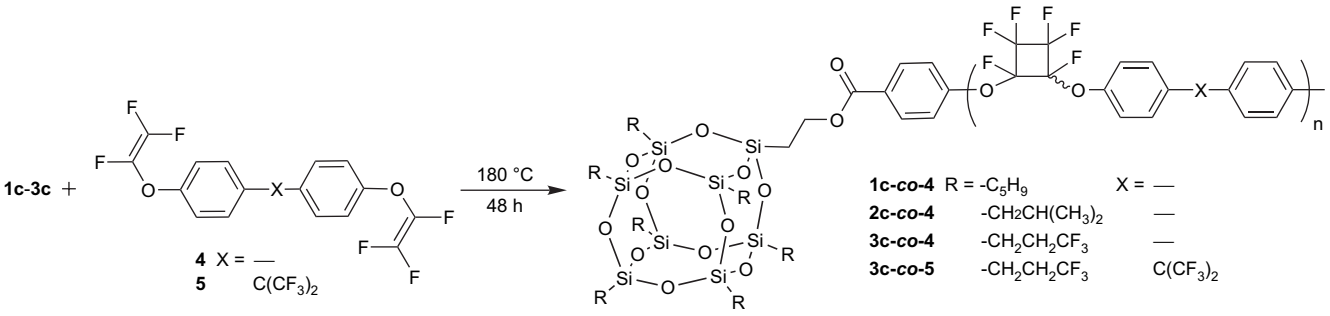
The overall four-step monomer synthesis produced good yields of 40–76% for **1c**–**3c**. Characterization and purity of POSS-functionalized TFVE monomers were confirmed by NMR ($^1H$, $^{13}C$, $^{19}F$, and $^{29}Si$), GPC, IR, and elemental analysis (C, H, and F). Sharp melting points at 75–77 °C were observed for monomers **2c** and **3c**; however, the cyclopentyl POSS-functionalized TFVE monomer **1c** showed no measurable melting <200 °C. All monomers are soluble in common polar and non-polar organic solvents (hexanes, THF, $CHCl_3$, acetone, and DMSO).

### 3.2. Polymerization

Copolymerization of POSS-functionalized PFCB monomers **1c**–**3c** with commercial bisfunctionalized TFVE monomer 4,4′-bis(4-trifluorovinyloxy)biphenyl (**4**) were performed in bulk at 180 °C for 48–96 h in vacuum-sealed ampoules (Scheme 3). Selected polymer properties are shown in Table 1. Copolymerization of **3c** with commercially available 2,2-bis(4-trifluorovinyloxybiphenyl)-1,1,1,3,3,3-hexafluoropropane (**5**) required extended heating at 180 °C for 96 h due to the established lower cyclodimerization rate for deactivated TFVE monomers [11a]. Polymers were purified by dissolving material in a minimal amount of THF, precipitated in MeOH, followed by filtration to afford fibrous yellow-white material.




Scheme 2. Synthesis of silsesquioxane-functionalized trifluorovinyl aryl ether monomers.




Scheme 3. Copolymerization of POSS-functionalized TFVE monomers **1c**–**3c** with bisfunctionalized TFVE monomers **4** and **5**.

In all cases, nearly quantitative weight recovery was observed for the purified polymers. Copolymer POSS incorporation was confirmed by $^{1}$H NMR analysis and agreed with calculated weight percents (Table 1).

$^{19}$F NMR was a diagnostic tool used to observe the conversion of TFVE monomers to PFCB polymers. The conversion of POSS-functionalized TFVE monomer **3c** to copolymer **3c-*co*-5** by $^{19}$F NMR is shown in Fig. 1. The diagnostic trifluorovinyl AMX pattern at −118.5 ($F_A$), −125.4 ($F_M$), and −134.5 ppm ($F_X$) converts to the perfluorocyclobutyl-$F_6$ multiplet at −127.2 to −132.8 ppm. Using either $^{1}$H or $^{19}$F NMR analysis, it was difficult to determine if POSS end groups were present on one or both ends of the linear polymer, albeit no terminal TFVE end groups were observed.

The cyclopentyl and *iso*-butyl endcapped POSS-functionalized copolymers **1c-*co*-4** and **2c-*co*-4** showed significantly lower $M_n$ values compared to homopolymer **poly4** (Table 1). This is possibly due to the high melting point (>200 °C) of monomer **1c** and its poor solubility in monomer **4** melt at bulk polymerization temperature of 180 °C. Similarly, the *iso*-butyl terminated POSS copolymer **2c-*co*-4** showed a factor of two lower $M_n$ compared with homopolymer **poly4** possibly due to increasing copolymer insolubility in the melt, however, still produced good film forming properties. GPC analysis illustrates the conversion of POSS-functionalized TFVE monomer **2c** to a monomodal distribution of **2c-*co*-4** as shown in Fig. 2. GPC traces of all crude copolymers showed no evidence of unreacted POSS-functionalized monomer. Clearly, from copolymers **1c-*co*-4** and **2c-*co*-4**, TFVE POSS monomers behave as chain terminators and they lower the $M_n$ compared with homopolymer **poly4**. On the other hand, the trifluoropropyl POSS copolymers **3c-*co*-4** and **3c-*co*-5** produced similar $M_n$ compared with **poly4** and **poly5**, respectively.

In all cases, the relative GPC $M_n$ appears to increase slightly within the copolymer series with increasing POSS monomer weight percent. This may be due to the increasing hydrodynamic volume due to bulky POSS cages appended to both single polymer chain ends. It should also be noted that solubility between biphenyl monomer **4** and fluorinated POSS monomer **3c** is dramatically increased over non-fluorinated POSS monomers. Therefore, the increase in relative

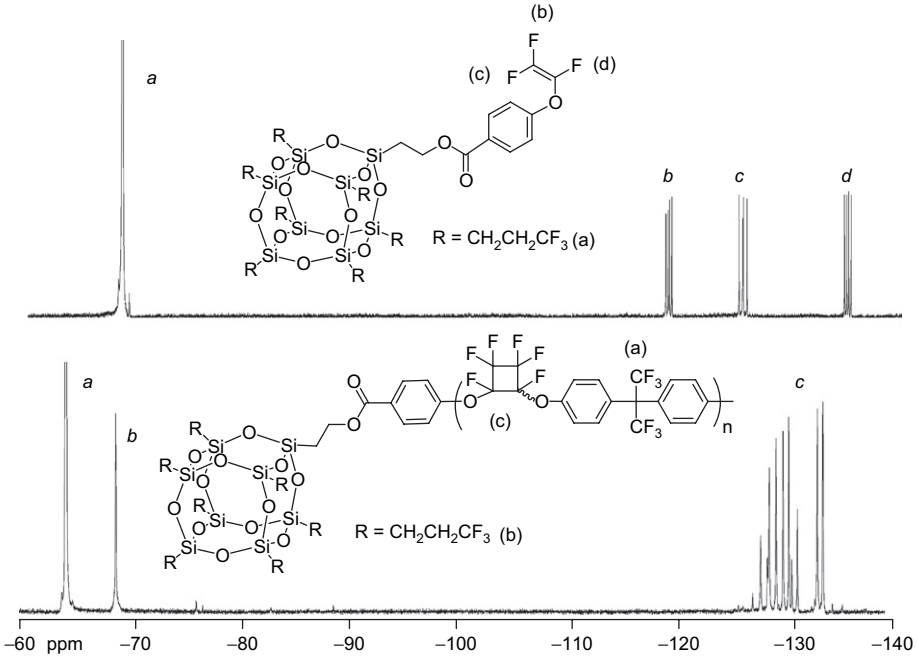



Fig. 1. $^{19}$F NMR (in $CDCl_3$) overlay of trifluorovinyl aryl ether-functionalized POSS **3c** (top) and 20 wt% POSS copolymer **3c-*co*-5** (bottom).

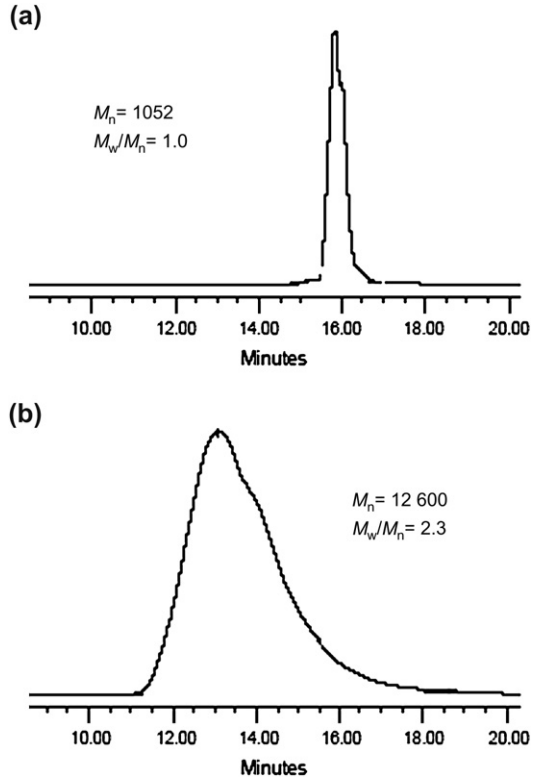



Fig. 2. Gel permeation chromatogram in $CHCl_3$ of TFVE POSS monomer **2c** (a) and copolymer **2c-*co*-4** with 20 wt% POSS (b).

GPC $M_n$ for the **3c** copolymer series could be attributed to both hydrodynamic volume increase and enhanced polymerization rate due to solubility. While most polydispersities were nearly the same for all copolymers compared with their respective homopolymers, copolymer **3c-*co*-4** showed the highest polydispersity and broadened with increased POSS content as expected from the increased conversion and higher molecular weight.

### 3.3. Thermal properties

Table 1 shows the DSC analysis of homopolymers and copolymers functionalized with POSS. Glass transition temperatures ($T_g$) for amorphous, semi-fluorinated PFCB homopolymers **poly4** and **poly5** were 140 and 97 °C, respectively. These values agree with previously reported work [3]. Increasing POSS content lowered $T_g$s in all copolymers and, for example, a 28% decrease in $T_g$ was observed for **2c-*co*-4** with 20 wt% POSS compared with homopolymer **poly4** (Fig. 3). Although, this observation may be attributed to low number-average molecular weight (particularly with **1c-*co*-4** and **2c-*co*-4**), incorporation of POSS does significantly affect $T_g$ since a PFCB homopolymer of **poly4** prepared with a comparable number-average molecular weight ($M_n$ of 13300) gave a similar $T_g$ of 139 °C. On the other hand, compatibility was observed using fluorinated POSS monomers in copolymer system **3c-*co*-4** with 10 wt% POSS and **3c-*co*-5** with 20 wt% POSS resulting in little deviation of $T_g$.

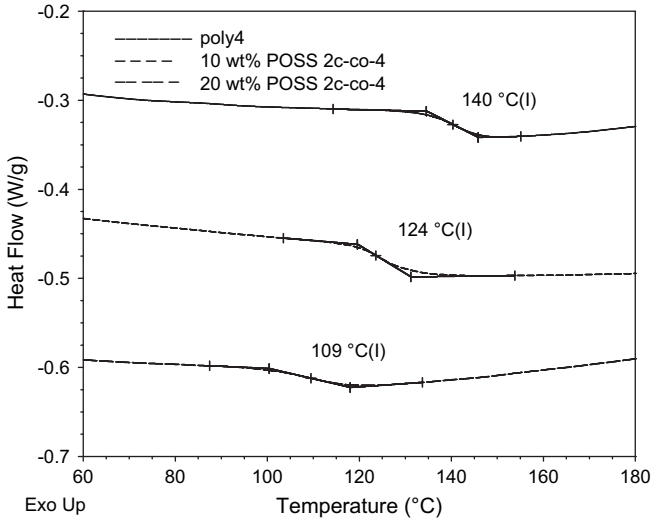



Fig. 3. DSC traces of homopolymer **poly4** and copolymer **2-*co*-4** with 10 and 20 wt% POSS.

### 3.4. Degradation analysis

Copolymer thermal stability was studied in nitrogen and air using thermo-gravimetric analysis (TGA) as shown in Table 2. Homopolymers **poly4** and **poly5** exhibit a high degree of thermal stability with recorded thermal decomposition temperatures ($T_d$) of 450 and 466 °C in nitrogen and 446 and 457 °C in air, respectively. For all copolymers studied, two onsets of degradation were observed in nitrogen and air. Fig. 4 illustrates the step-wise decomposition of POSS PFCB copolymer **2c-*co*-4** in comparison with the homopolymer **poly4**. TGA showed the onset of degradation in nitrogen and air results in a weight loss proportional to the weight percent of POSS content in the copolymers.

The comparison of GC–MS pyrolysis analysis of monomer **1c** with **1c-*co*-4** revealed evidence of similar POSS cage decomposition to siloxane fragments. This fragmentation pattern showed $[M]^+$ with *m/z* (relative intensity): 284 (53%), 249

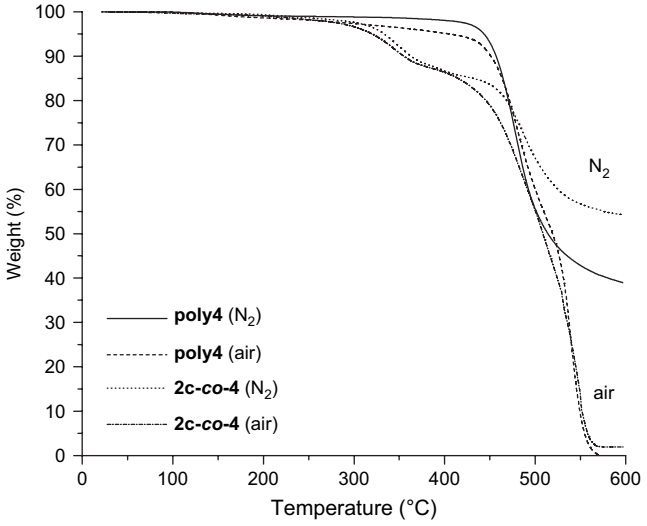



Fig. 4. TGA comparison of homopolymer **poly4** and copolymer **2-*co*-4**.

(12%), 214 (7%), 142 (15%), 107 (8%), 71 (5%). Molecular weights (*m*/*z*) of 284, 214, and 142 primarily allude to siloxane fragments of $[(C_5H_9SiO)_2SiCH_2CH_2]^+$, $[(C_5H_9Si)_2O]^+$, and $[C_5H_9SiO_3]^+$, respectively. The main components of GC analysis for **1c-*co*-4** produced phenolic species as a result of expulsion of the hexafluorocyclobutene from the PFCB ring. This has been previously shown by Babb et al. based on the thermal degradation of PFCB polymers [10]. TGA analysis showed a significant increase in final decomposition temperature ($T_d > 500$ °C) of copolymers **1c-*co*-4** with 20 wt% POSS (in nitrogen) and **2c-*co*-4** with 10 and 20 wt% POSS (in nitrogen and air) relative to the PFCB homopolymer **poly4**. In most other cases, a modest increase in final $T_d$ was observed for copolymers containing POSS. POSS has been shown to improve polymer thermal stability [19], possibly by a self-passivating mechanism ultimately creating silicon oxide layer [20]. Char yields were in the range of 11–54% in nitrogen at 600 °C for all copolymers studied using TGA analysis; no char was observed by measurements performed in air at that temperature.

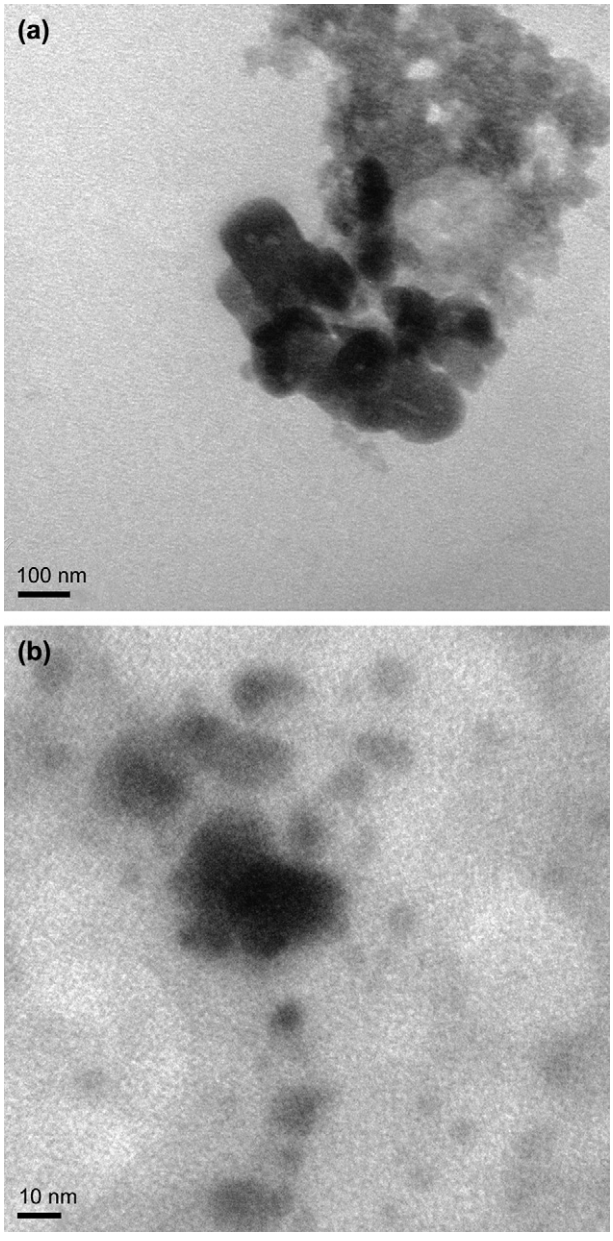



Fig. 5. TEM images of **2c-*co*-4** with 20 wt% POSS illustrating POSS aggregates as darkened areas.

### 3.5. Surface analysis of copolymers

Films of the copolymers were prepared from spin casting using a minimal amount of THF (approximately 80 wt% solids) producing 3–5 μm thick films. The films produced were transparent and flexible. Initial surface characterization using SEM showed no micron-sized POSS aggregates; however, the use of TEM revealed the presence of 50–150 nm POSS clusters confirmed by energy dispersive X-ray spectroscopy (EDS) (Fig. 5). These POSS clusters were observed on various areas on the TEM grid and best represent that of the entire sample.

## 4. Conclusions

A new PFCB polymer endcapped with POSS has been prepared through the facile functionalization of commercial POSS triols and commercial TFVE intermediates. The copolymers exhibited moderate to high molecular weight, lower $T_g$s, and gave transparent creasable spin cast films with excellent solvent processability. In some cases, the copolymers functionalized with POSS produced a higher degree of stability in nitrogen and air. We anticipate this new class of POSS-functionalized PFCB polymers for use as a versatile material in a multitude of high performance fluoropolymer applications requiring processability and high thermal resistance.

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